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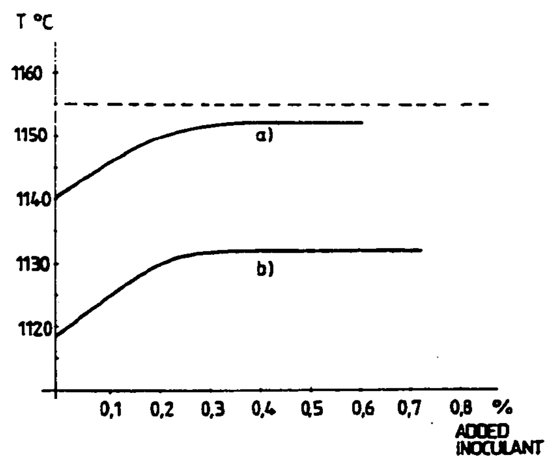
(54) Title: A METHOD FOR CONTROLLING AND REGULATING THE PRIMARY NUCLEATION OF IRON MELTS



(57) Abstract

The invention relates to a method of regulating the solidification process in iron casting operations. This is effected by determining the intrinsic crystallisation ability of a base melt and modifying the same. A sample is taken from the base m lt in a sample vessel which is in thermal equilibrium with the sample melt before solidification commences. The sample vessel is provided with at least one thermoelement and contains a given and calibrated quantity of inoculant on FeSi-base, this quantity being sufficient to provide a maximum inoculating effect. The sample melt is all wed t s lidify and the difference between the lowest temperature in the undercooling phase prior to the eutectic reaction and the maximum temperature in the eutectic reaction phase and the eutectic equilibrium temperature is determined. When this difference exceeds 10 K and 5 K respectively, thermodynamically stable particles of the type spinels or oxysulphides of elements such as magnesium, calcium, zirconium, strontium, titanium and rare earth metals, are added to the melt. These procedural steps may be repeated until the temperature differences fall below the aforesaid limits.

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A method for controlling and regulating the primary nucleation of iron melts

The present invention relates to a method for controlling the solidification process of a casting melt, by determining the intrinsic crystallisation ability of a melt and making those corrections that are necessary.

When producing cast iron of all conceivable types, it is very important to check the number of graphite crystals formed per unit of volume. In white cast iron no graphite crystals are formed; mottled cast iron has a few graphite crystals; grey cast iron and cast iron with compact graphite have a moderate number of graphite crystals; and nodular iron normally has a large number of graphite crystals.

Consequently, a nucleation stimulant is introduced into the melt shortly before the casting process, in order to stimulate the formation of a desired number of graphite crystals. A large number of nucleation stimulants are commercially available, the majority of these stimulants being based on ferrosilicon (FeSi) or silicon carbide. Many of these stimulants contain so-called inoculating agents and also certain additive elements, such as calcium, strontium or zirconium, with the intention of amplifying the effect of the stimulants.

The effect produced by the inoculating agents is very shortlived, however, and these agents must therefore be added to the melt at a late stage of the casting process, often in the casting jets or even in the actual casting mould itself. It is obvious that the effect of such additives is difficult to monitor and control in a manner to achi ve optimal r sults, since the

inoculating effect achieved will vary from melt to melt, and therewith from product to product.

The mechanism through which nucleation of graphite crystals takes place in the presence of FeSi-particles (the substance is most normally added in the form of coarse granules having a size of 1-10 mm) is well described in the literature (see for instance Ch Wang and Fredrikson; 48th International Casting Congress in Varna, Bulgaria, 1981-10-4--7, 255).

The carbon equivalent (i.e. C.E. = % C + % Si/4) will increase sufficiently in the diffusion zone that occurs when an FeSi-particle is dissolved in the melt for a graphite crystal to graphitize in the melt, provided that this small graphite crystal survives until its normal growth temperature has been reached (i.e. generally at a temperature < 1155°C). Under such circumstances, the graphite crystal is able to develop to a flaky graphite crystal or a graphite nodule, depending upon the chemical environment prevailing in the iron melt. Whereas Wang and Fredrikson state that the formation of graphite crystals takes place through an homogenous nucleation process, several other authors, for instance Jacobs et al, Metals Technology, March 1976, page 98 (page 102) state the opinion that the formation of graphite crystals is a heterogenous nucleation process. These authors have namely found in graphite crystals primary crystallisation nuclei which consist of complex oxides of such elements as calcium, magnesium and aluminium of the spinel type, which are thermodynamically stable and well dispersed in the melt. The present invention is based on the significance of these so-called primary nuclei.

The concentration of such primary nuclei in the base melts used in present day casting technology varies considerably, partly due to the starting material used; this starting material ranges from sponge iron, material recycled from the foundry concerned, to steel scrap and more or less well defined scrap purchased on the market.

The melting method used also plays an important part. Furnaces operate in accordance with different principles (for instance gas-fired or oil-fired cupola furnaces, light-arc furnaces and induction furnaces), which heat the base iron to different temperatures during the melting process. Furthermore, the furnace linings influence the sulphide, oxysulphide and oxide particles in the molten material. Consequently, the concentration of primary nuclei in the base melt will vary very widely, not solely from the one production line to the other, but also from batch to batch in one and the same production line.

It is known many patent specifications disclose valuable information concerning the properties of a melt. SE-B-350 606 in particular teaches a method in which a sample of the melt is taken in a sampling vessel when casting aluminium and the temperature changes that take place in time as the melt solidifies are recorded with the aid of a thermoelement placed in the melt. These records are then used to anticipate crystallisation conditions on the basis of undercooling values, the slope of different parts of the curve, and constant temperatures during the eutectic reaction. SE-B-444 817 teaches a method by means of which information concerning the properties of the melt can be obtained such as to be able to determine whether the melt will solidify

as flaky graphite iron, as a compact graphitic iron or as nodular iron.
This information is obtained with the aid of two thermoelements, one of which is placed in the melt in the centre of a sampling vessel and the other is placed in the melt in the proximity of the wall of said vessel.

According to the present invention there is provided a method for regulating the solidification process in the casting of iron, this method comprising the steps of determining the intrinsic crystallisation ability of a base iron melt and modifying this ability, said method being characterized by taking a melt sample in a sampling vessel which is in thermic equilibrium with the sample quantity prior to solidification commencing, said sampling vessel having been provided with at least one thermoelement and containing a determined and calibrated quantity of inoculating agent based on FeSi and sufficient to produce a maximum inoculating effect; allowing the sample melt to solidify while recording temperature changes per unit of time; determining the difference between the minimum temperature in the undercooling phase, the maximum temperature in the eutectic reaction phase, and the eutectic equilibrium temperature T_e; adding to the base melt thermodynamically stable particles of the type spinels or oxysulphides of elements such as magnesium, aluminium, potassium, zirconium, strontium, titanium and rare earth metals when the difference between eutectic equilibrium temperature T_e and the minimum temperature in the undercooling phase exceeds 10 K and when the difference between T_e and the maximum temperature in the eutectic reaction phase exceeds 5 K; and if found suitable repeating these method steps until the aforesaid difference falls beneath 10 K and 5 K

respectively.

The formation of oxides and/or oxysulphides is promoted when sulphides are present in the melt, such as manganese sulphide. The oxides may be of the spinel type, for instance spinel $MgAl_2O_4$, or of the oxysulphide type, such as Ce_2O_2S.

When only one inoculant, such as FeSi, is added to a base graphite iron melt which contains only a very small amount of primary nuclei, practically no inoculating effect is obtained. The same applies when an inoculant consisting of spinels and/or oxysulphides is added to this base melt. However, if the relatively stable spinels and/or oxysulphides are added first and FeSi is added thereafter in conjunction with the casting process, a desired, controlable inoculating effect is obtained.

The inoculant added to the sampling vessel in a calibrated and determined quantity is preferably a known, commercially available inoculant, such as an inoculant of the type known as "Superseed", having a particle size of from 2-4 mm. The amount of inoculant added shall correspond, for instance, to 0.2% of the total weight of the sample, subsequent to filling the sampling vessel with molten iron to the rim of said vessel. The minimum temperature during the undercooling phase which releases the eutectic reaction, and the maximum temperature during the eutectic reaction, are then determined with the aid of temperature measuring deviecs, preferably thermoelements, placed in the sampling vessel. The melt will contain a sufficient number of primary crystallisation nuclei when the minimum temperature is less than 10 K beneath the

equilibrium temperature. In this context, the eut ctic temperature has been defined as 1150°C and the thermo-elements have been calibrated accordingly.

If the measured minimum temperature is beneath these defined temperature limits, it is necessary to add a given, calibrated amount of primary nuclei to the melt. As a rule of thumb, it can be said that the amount of primary nuclei added to the melt is doubled for each further 5 K interval by which the measured eutectic reaction temperature falls beneath the eutectic equilibrium temperature.

The method by which crystallisation nuclei are added can vary. Oxides and oxysulphides can be introduced to the melt through the medium of suitable fluxes, although a better result is obtained when the stable particles are formed directly in the melt to achieve optimal dispersion and wetting. Calcium, aluminium, magnesium, strontium, zirconium, cerium or other rare earth metals in elementary form can be introduced in accordance with injection metallurgical principles with the aid of an inert carrier gas containing a measured amount of oxygen, or metal powder can be mixed with a readily disassociated oxide, such as iron oxide, and introduced into the base melt in the casting stream or jet when transferring the melt to a holding furnace, or with the aid of a dipping ladle in the holding furnace. A more sophisticated method is one in which powder is enclosed in a tube of appropriate diameter and fed into the melt with the aid of a wire feeder.

Because of the high carbon activity, and therewith low oxygen potential, it may be difficult at times to achieve an effective oxide formation of the kind

desired, by introducing additives directly to a cast iron melt.

One alternative is then to produce a master alloy having a high content of oxide/oxysulphide particles from a separate melt having a low carbon content, and to dilute this master alloy in the melt to be treated. This master alloy, which will preferably contain at least 100 times the desired final particle concentration, can be produced in different solid forms, for instance in pellet form or in the form of small moulded pieces or in wire form, and can be introduced into the melt with the aid of suitable devices.

The master alloy used will preferably contain less than 5% of metals other than iron, thus more than 95% iron, and is preferably introduced to the molten iron in a quantity smaller than 1% of the total amount of cast iron.

A master alloy is produced by adding the desired metals present in oxides or oxysulphides in an environment such that oxidation with oxygen or sulphur will take place, and consequently the carbon content should be as low as possible in order to prevent carbon present in the melt from having a negative influence on the oxidation process.

As beforementioned, when practising the inventive method undercooling is measured with the aid of at least one thermoelement placed in the sample quantity taken from the melt. In this respect, it has been found important to use two thermoelements, one placed in the centre of the sample melt and the other close to the inner surface of th sample vessel wall, wherein th

difference between the minimum temperature in the undercooling phase for the eutectic reaction and the eutectic equilibrium temperature is determined with the aid of the thermoelement placed in the proximity of the inner surface of the sample vessel. The difference between the eutectic equilibrium temperature and the maximum temperature in the eutectic reaction phase is determined with the aid of the thermoelement placed in the centre of the sample. Should inverse segregation take place to an extent such that exudation of melt occurs, this can be observed from the rapid increase in temperature that takes place in the melt and recorded on the thermoelement positioned close to the inner surface of the sample vessel. The occurrence of exudation is evidence of the fact that the melt is deficient in crystallisation nuclei. Consequently, thermodynamically stable particles of the type spinels or oxysulphides must be added to the melt in quantities larger than those otherwise motivated by the minimum temperature of the undercooling phase measured in the centre of the sample vessel. The sampling process can then be repeated until the exudation phenomenon ceases and the aforesaid temperature differences lie between 10 K and 5 K respectively. Exudation is essentially due to a deficiency of crystallisation nuclei in the melt, and when a skin of solidified iron is formed at the inner surface of the sample vessel, the skin will contract and the melt located inwardly of the skin will penetrate the skin and cause molten metal to be pressed out through the skin wall. The thermoelement positioned adjacent the inner wall of the sample vessel will therewith register an elevated temperature.

One important advantage afforded by the inventive method is that a base-inoculant of an FeSi-type can be

used in combination with a modifying agent of the spinel or oxysulphide type. The base-inoculant is relatively inexpensive in comparison with a modifying inoculant.

The following series of tests illustrate how the effect of inoculant additions can vary from one production line to another. This variation is shown in Figure 1, which illustrates the effect obtained when adding an amount of inoculant to the melt, and also shows the minimum undercooling temperature which precedes the eutectic reaction.

Different quantities of a commercially available inoculant of the FeSi-type with an addition of strontium, "Superseed", were added to a base iron.

a) <u>A base iron containing a sufficient quantity of primary nuclei</u>

A thermoanalysis of the undercooling temperature prior to the eutectic reaction gave the measurement values disclosed in Figure 1, where the minimum temperature is plotted as a function of the amount of inoculant added, expressed in percent by weight of the sample melt. It will be seen from curve a) that a full inoculating effect was measured with an addition of 0.2% inoculant and that the minimum temperature lies close to the eutectic equilibrium temperature, i.e. 1150-1155°C. A metallographic examination showed fully developed A-graphite or flaky graphite throughout the whole of the sample volume.

b) <u>A base iron with an insufficiency of primary nuclei</u>

The same type of inoculant was added as that according to curve a) above, although in this case the addition

was made to a base iron melt having an insufficiency of primary nuclei, as illustrated in curve b), the minimum temperature in this case lying on a much lower level. The minimum temperature of the eutectic reaction will never reach those values characteristic of a well inoculated material of A-graphite type, irrespective of the amount of inoculant added. When adding 0.25% inoculant, the samples, when examined metal-lographically, showed a relative quantity of D-graph-ite, "undercooled graphite", reaching to 40-60% of the total amount of graphite in the sample.

It will be seen from the curves in Figure 1 that an addition of a given inoculant of the FeSi-type in quantities above 0.2% will not appreciably influence the inoculating effect.

It is possible on the basis hereof to devise a simple measuring method by means of which the concentration of primary crystallisation nuclei in the melt can be established. This measuring or assaying procedure is effected by first introducing a molten inoculant of the FeSi-type into the sample melt in an amount correspond-ing to at least 0.2%, and thereafter recording the minimum temperature prior to the eutectic reaction and the maximum temperature at the eutectic reaction and comparing the values obtained with the eutectic equi-librium temperature.

The concentration of primary crystallisation nuclei in the melt can then be adjusted, in accordance with the invention, so that conditions which are optimum for graphite precipitation in the melt casting process are obtained.

CLAIMS

1. A method for controlling the solidification process in iron casting operations, comprising the steps of determining the intrinsic crystallisation ability of a base iron melt and modifying said ability, c h a r a c t e r i z e d by taking a melt sample in a sampling vessel which is in thermic equilibrium with the sample quantity prior to solidification commencing, said sampling vessel having been provided with at least one thermoelement and containing a determined and calibrated quantity of inoculating agent based on FeSi and sufficient to produce a maximum inoculating effect; allowing the sample melt to solidify while recording temperature changes per unit of time; determining the difference between the minimum temperature in the undercooling phase, the maximum temperature in the eutectic reaction phase, and the eutectic equilibrium temperature T_e; adding to the base melt thermodynamically stable particles of the type spinels or oxysulphides of elements such as magnesium, aluminium, potassium, zirconium, strontium, titanium and rare earth metals when the difference between eutectic equilibrium temperature T_e and the minimum temperature in the undercooling phase exceeds 10 K and when the difference between T_e and the maximum temperature in the eutectic reaction phase exceeds 5 K; and if found suitable repeating these method steps until the aforesaid difference falls beneath 10 K and 5 K respectively.

2. A method according to Claim 1, c h a r a c t e r i z e d by introducing the inoculant on an FeSi-base in a determined and calibrated quantity of such magnitude that the inoculant content of the melt accommodated in the sample vessel will be at least 0.2% percent by weight.

3. A method according to Claim 1, c h a r a c t e r i z e d in that thermodynamically stable particles of the type spinels or oxysulphides are delivered to the melt by immersing into said melt a wire or rod which consists of at least one outer layer of iron which encloses one or more of the metals calcium, magnesium, aluminium, zirconium, strontium, titanium and rare earth metals, and a readily disassociated oxide, such as iron oxide, in metallic form.

4. A method according to Claim 1, c h a r a c t e r i z e d in that the supply of thermodynamically stable particles of the type spinels or oxysulphides is effected by injecting calcium, magnesium, aluminium, zirconium, titanium, strontium or rare earth metals into the melt with an inert gas, together with an oxidizing agent.

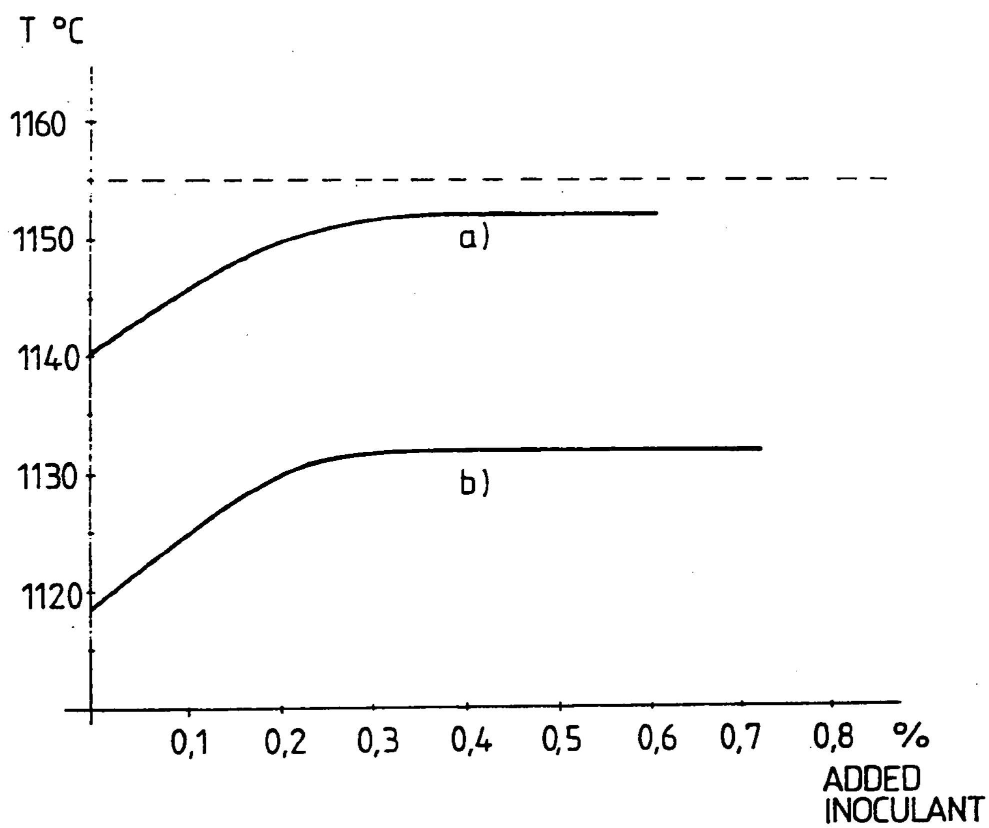
5. A method according to Claim 4, c h a r a c t e r i z e d in that the oxidizing agent is a readily disassociated oxide.

6. A method according to Claim 4, c h a r a c t e r i z e d in that the oxidizing agent is an oxygen gas or air.

7. A method according to Claim 1, c h a r a c t e r i z e d in that registration of temperature changes per unit of time is effected in the centre of the sample melt and in the vicinity of the inner surface of the sample vessel, wherein the difference between the minimum temperature in the undercooling phase prior to the eutectic reaction and the eutectic equilibrium temperature is determined with the aid of a thermoelement positioned adjacent the inner wall of said sample vessel, and the difference between the eutectic equilibrium temperature and the maximum temperature in the eutectic reaction phase is determined in the centre of the sample melt and that the occurrence of inverse segregation of such magnitude that exudation of the melt occurs is determined by registering a rapid rise in temperature by the thermal element positioned adjacent the inner surface of the vessel; and in that when exudation is registered large quantities of thermodynamically stable particles of the type spinels or oxysulphides are added to the sample melt; and in that the above procedural steps are repeated until said differences are smaller than 10 K and 5 K respectively and no exudation is registered.

8. A method according to Claim 1, c h a r a c t e r i z e d by introducing primary nucleating particles through the medium of a master alloy which is produced separately by forming oxides/oxysulphides of elements such as Cu, Mg, Al, Zr, Sr, Ti and rare earth metals in a melt having low carbon activity and in a substasntially high concentration, said master alloy being introduced into the melt to be treated in a manner known per se.

9. A method according to Claim 8, c h a r a c - t e r i z e d in that the master alloy contains more than 95% iron.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INTERNATIONAL SEARCH REPORT

International Application No PCT/SE 91/00144

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 21 C 1/08, C 22 C 33/08

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	C 21 C; C 22 C; G 01 N

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]

SE,DK,FI,NO classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

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A	US, A, 4046509 (STIG LENNART BÄCKERUD) 6 September 1977, see column 4, line 62 - column 6, line 2 --	1,7
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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
21st May 1991	1991 -05- 31
International Searching Authority	**Signature of Authorized Officer**
SWEDISH PATENT OFFICE	Nils Engnell Nils Engrell

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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.PCT/SE 91/00144

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
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